Influence of substituents on cation-anion contacts in imidazolium perrhenates

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Electronic Supporting Information

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1. X-ray crystallography

1.1. Measurement details

Table S1. Crystallographic data for compounds **1-6.**

	1	**2**	**3**	**4**	**5**	**6**
CCDC	1030631	1030632	1030633	1030634	1030635	1030636
formula	$C_{11}H_{13}N_2O_4Re$	$C_{12}H_{15}N_2O_4Re$	$C_{13}H_{17}N_2O_4Re$	$C_{14}H_{19}N_2O_4Re$	$C_{11}H_8F_5N_2O_4Re$	$C_{12}H_{10}F_5N_2O_4Re$
fw	423.44	437.47	451.50	465.52	513.40	527.43
colour/habit	clear colourless block	clear colourless prism	colourless needles	clear colourless fragment	yellow fragment	clear colourless fragment
cryst dimensions (mm^3)	0.104 × 0.136 × 0.205	0.11 × 0.18 × 0.23	0.090 × 0.231 × 0.246	0.149 × 0.161 × 0.216	0.20 × 0.25 × 0.30	0.11 × 0.13 × 0.26
cryst syst	orthorhombic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P\,2_1\,2_1\,2_1$	$P\,\bar{1}$;	$P\,b\,c\,a$	$P\,2_1/n$	$P\,2_1/n$	$C\,2/c$
a, Å	5.8129(1)	8.0076(5)	11.0896(2)	12.2997(3)	8.0372(2)	13.1970(2)
b, Å	11.4171(1)	9.4780(5)	14.4508(2)	8.3808(2)	10.1535(2)	9.4355(2)
c, Å	19.4879(3)	10.6971(6)	18.4542(3)	16.4451(3)	17.2223(3)	24.8443(5)
α, deg	90	65.571(2)	90	90	90	90
β, deg	90	77.076(2)	90	111.587(1)	90.5967(8)	96.309(1)
γ, deg	90	68.508(2)	90	90	90	90
V, $Å^3$	1293.34(3)	685.29(7)	2957.35(8)	1576.28(6)	1405.36(6)	3074.88(10)
Z	4	2	8	4	4	8
T, K	123(2)	123(2)	123(2)	123(2)	123(2)	100(2)
D_{calcd}, g cm^{-3}	2.175	2.120	2.028	1.962	2.427	2.279
μ, mm^{-1}	9.403	8.877	8.232	7.725	8.726	7.980
F(000)	800	416	1728	896	960	1984
ϑ range, deg	2.07 – 30.58	2.10 – 25.38	2.21 – 25.37	2.59 – 33.20	2.33 – 25.41	1.65– 25.39
Index ranges (h, k, l)	-7 – 8, ±16, ±27	±9, ±11, ±12	-10 – 13, ±17, -21 – 22	±18, ±12, ±25	±9, ±12, ±20	±15, ±11, ±29
no. of rflns collected	13584	17956	19638	77447	38559	46517
no. of indep rflns/R_{int}	3972/0.0284	2508/0.0518	2712/0.0402	6016/0.0379	2592/0.0233	2833/0.0435
no. of obsd rflns (I>2σ(I))	3799	2491	2201	5165	2565	2472
no. of data/restraints/params	3972/0/164	2508/0/174	2712/0/183	6016/0/193	2592/0/241	2833/0/219
R1/wR2 (I>2σ(I))[a]	0.0183/0.0314	0.0150/0.0386	0.0187/0.0366	0.0182/0.0347	0.0135/0.0316	0.0168/0.0352
R1/wR2 (all data)[a]	0.0203/0.0319	0.0151/0.0387	0.0282/0.0395	0.0260/0.0367	0.0138/0.0317	0.0226/0.0367
GOF (on F^2)[a]	0.985	1.218	1.008	1.023	1.241	1.058
Largest diff peak and hole (e $Å^{-3}$)	+0.642/-0.591	+0.632/-0.568	+0.460/-0.534	+1.052/-0.999	+0.574/-0.374	+1.644/-0.612

[a] $R1 = \sum(||F_o|-|F_c||)/\sum|F_o|$; $wR2 = \{\sum [w(F_o^2-F_c^2)^2]/ \sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

Table S2. Crystallographic data for compounds **7-11.**

	7	**8**	**9**	**10**	**11**
CCDC	1030637	1030638	1030639	1030640	1030641
formula	$C_{13}H_{12}F_5N_2O_4Re$	$C_{14}H_{14}F_5N_2O_4Re$	$C_{17}H_{17}N_2O_4Re$	$C_{17}H_{12}F_5N_2O_4Re$	$C_{17}H_7F_{10}N_2O_4Re$
fw	541.46	555.48	499.54	589.50	679.46
colour/habit	clear colourless block	clear colourless block	colourless fragment	yellow fragment	clear colourless prisma
cryst dimensions (mm^3)	0.09 × 0.10 × 0.19	0.21 × 0.31 × 0.39	0.15 × 0.20 × 0.20	0.43 × 0.47 × 0.98	0.11 × 0.14 × 0.52
cryst syst	orthorhombic	orthorhombic	triclinic	monoclinic	orthorhombic
space group	$P\,n\,a\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,\bar{1}$;	$P\,2_1/n$	$P\,2_1\,2_1\,2_1$
a, Å	10.3689(3)	9.6255(3)	7.7420(3)	8.3467(2)	6.5996(2)
b, Å	18.6571(7)	11.6206(4)	9.7001(3)	10.5776(3)	12.4519(3)
c, Å	8.4223(3)	15.4559(5)	12.1493(4)	20.3571(6)	23.9499(6)
α, deg	90	90	77.4846(14)	90	90
β, deg	90	90	85.3240(14)	100.458(1)	90
γ, deg	90	90	72.6881(13)	90	90
V, $Å^3$	1629.32(10)	1728.81(10)	850.22(5)	1767.43(8)	1968.14(9)
Z	4	4	2	4	4
T, K	123(2)	123(2)	173(2)	123(2)	123(2)
D_{calcd}, g cm^{-3}	2.207	2.134	1.951	2.215	2.293
μ, mm^{-1}	7.533	7.102	7.169	6.955	6.297
$F(000)$	1024	1056	480	1120	1280
ϑ range, deg	2.18 – 26.36	2.19 – 33.11	1.72 – 25.51	2.03 – 25.55	1.84 – 34.71
Index ranges (h, k, l)	±12, ±23, ±10	±14, ±17, ±23	±9, ±11, ±14	±10, ±12, ±24	±10, ±19, ±38
no. of rflns collected	46035	85286	29374	33118	66878
no. of indep rflns/R_{int}	3328/0.1170	6533/0.0676	3159/0.0402	3295/0.0277	8440/0.0389
no. of obsd rflns ($I>2\sigma(I)$)	2686	6286	3078	3186	7892
no. of data/restraints/params	3328/1/229	6533/0/236	3159/0/285	3290/0/311	8440/0/307
R1/wR2 ($I>2\sigma(I)$)[a]	0.0287/0.0441	0.0205/0.0470	0.0196/0.0519	0.0131/0.0290	0.0185/0.0351
R1/wR2 (all data)[a]	0.0442/0.0478	0.0221/0.0474	0.0203/0.0524	0.0140/0.0293	0.0219/0.0358
GOF (on F^2)[a]	0.974	1.032	1.089	1.165	1.017
Largest diff peak and hole (e $Å^{-3}$)	+0.925/-0.612	+1.293/-1.351	+1.373/-1.405	+0.425/-0.320	+0.926/-0.502

[a] $R1 = \sum(||F_o|-|F_c||)/\sum|F_o|$; $wR2 = \{\sum [w(F_o^2-F_c^2)^2]/ \sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

1.2. Molecular structures of compounds 1–11

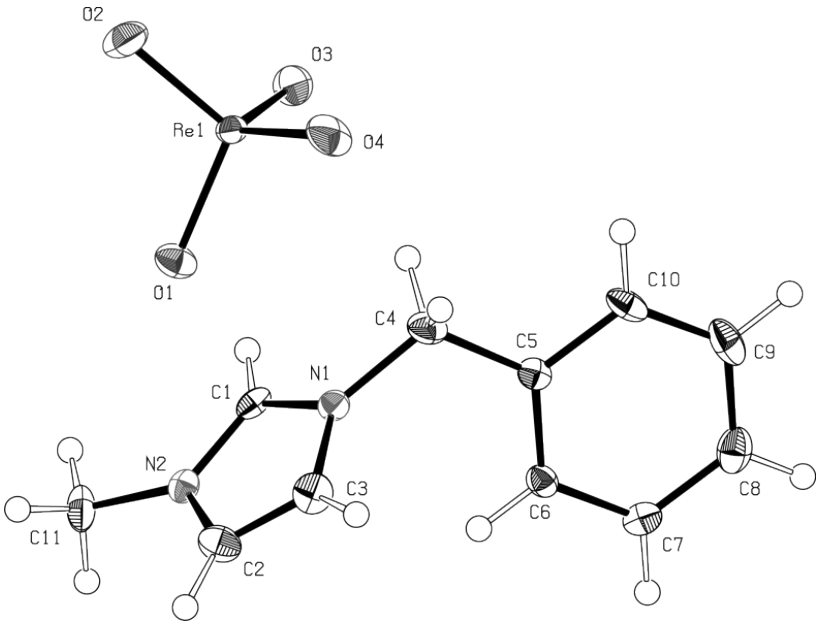


Figure S1. ORTEP style plot of compound **1** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.729(3), Re1–O2 1.727(3), Re1–O3 1.721(3), Re1–O4 1.723(3); O3–Re1–O4 110.39(16), O3–Re1–O2 109.53(13), O4–Re1–O2 110.10(16), O3–Re1–O1 109.46(14), O4–Re1–O1 108.86(13), O2–Re1–O1 108.48(14).

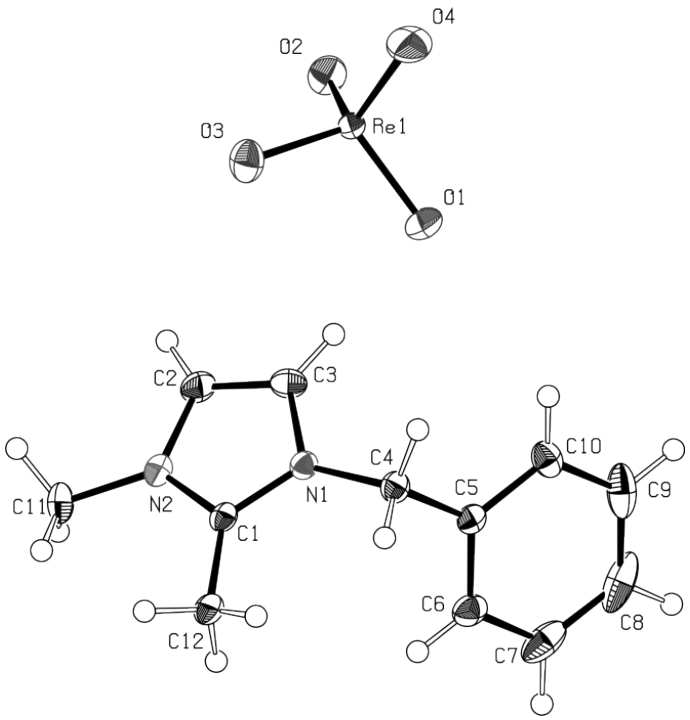


Figure S2. ORTEP style plot of compound **2** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.720(2), Re1–O2 1.728(2), Re1–O3 1.719(2), Re1–O4 1.721(2); O3–Re1–O4 109.81(12), O3–Re1–O2 109.55(11), O4–Re1–O2 109.87(12), O3–Re1–O1 109.22(11), O4–Re1–O1 109.42(11), O2–Re1–O1 108.95(11).

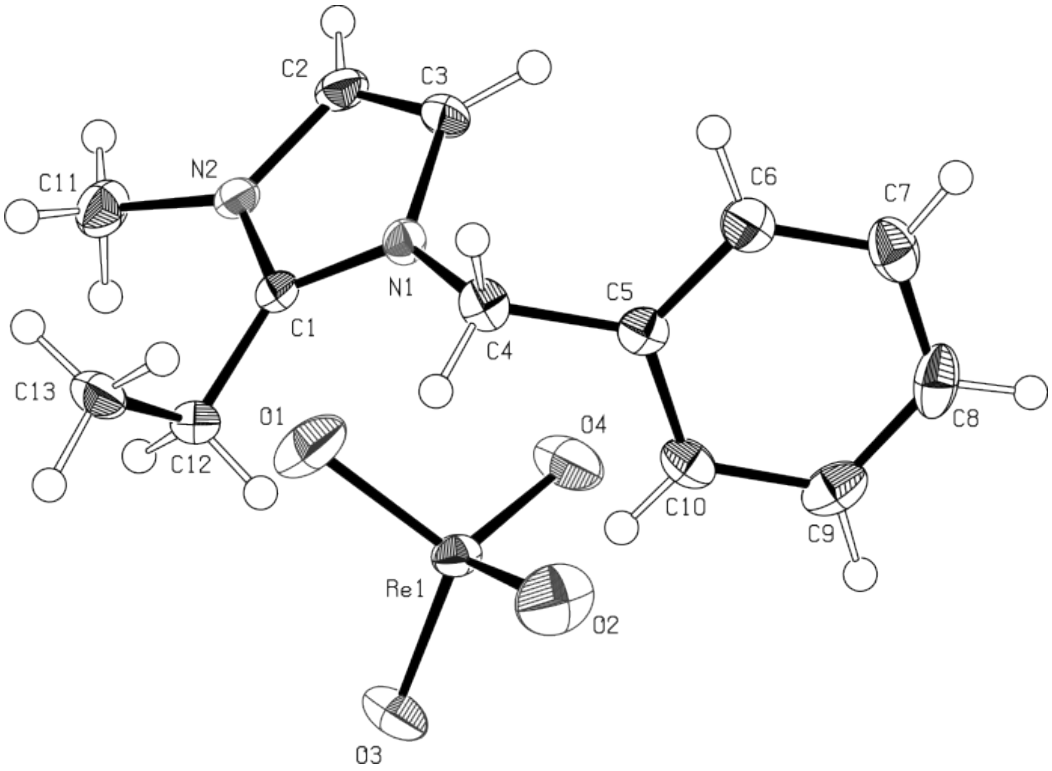


Figure S3. ORTEP style plot of compound **3** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.714(3), Re1–O2 1.706(3), Re1–O3 1.722(2), Re1–O4 1.718(3); O1–Re1–O2 110.95(14), O1–Re1–O3 109.48(13), O1–Re1–O4 108.85(14), O2–Re–O3 109.56(13), O2–Re1–O4 109.00(14), O3–Re1–O4 108.95(12).

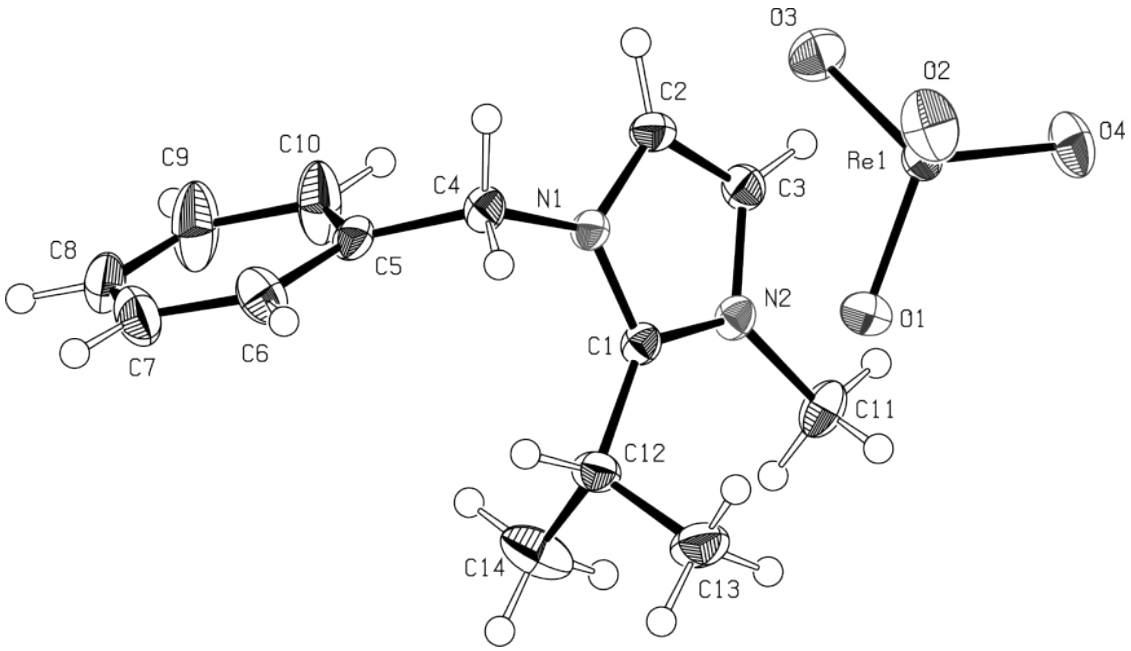


Figure S4. ORTEP style plot of compound **4** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.7149(15), Re1–O2 1.7267(15), Re1–O3 1.7217(15), Re1–O4 1.7233(14); O1–Re1–O2 109.57(9), O1–Re1–O3 108.83(8), O1–Re1–O4 109.71(8), O2–Re–O3 109.41(8), O2–Re1–O4 110.16(8), O3–Re1–O4 109.13(8).

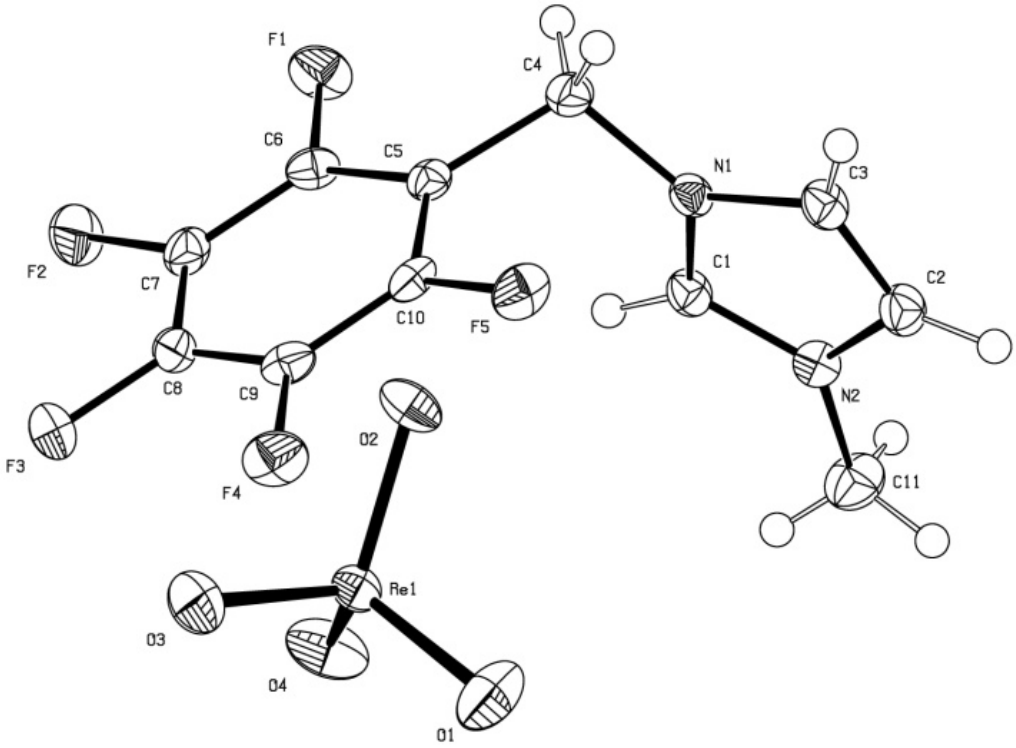


Figure S5. ORTEP style plot of compound **5** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O4 1.731(2), Re1–O3 1.720(2), Re1–O1 1.716(2), Re1–O2 1.730(2); O1–Re1–O3 109.32(11), O1–Re1–O4 109.22(11), O2–Re1–O3 108.85(10), O2–Re1–O4 108.94(11), O3–Re1–O4 110.03(11), O1–Re1–O2 110.48(10).

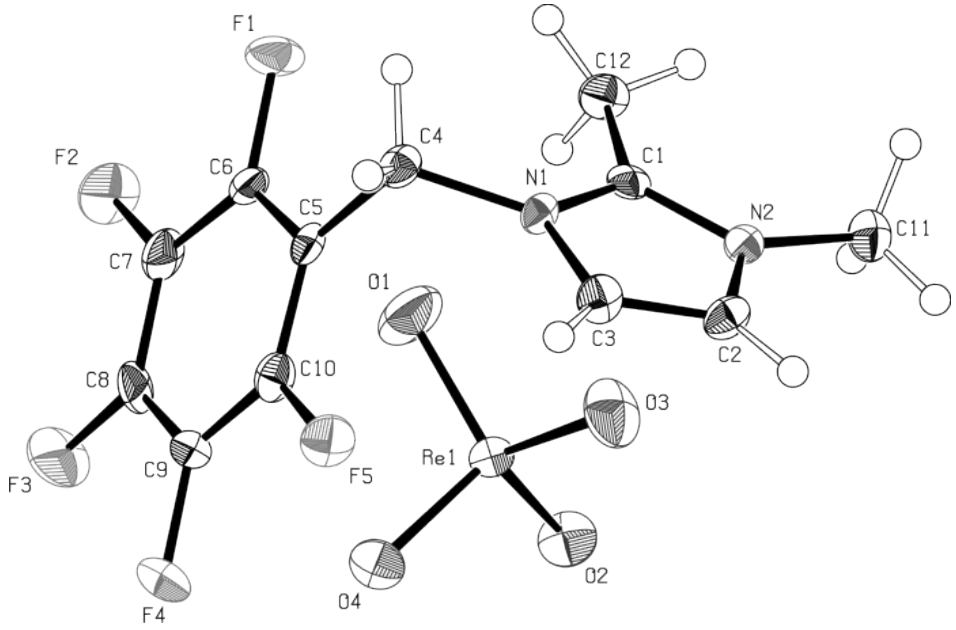


Figure S6. ORTEP style plot of compound **6** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.708(3), Re1–O2 1.726(3), Re1–O3 1.716(3), Re1–O4 1.724(2); O1–Re1–O2 110.69(14), O1–Re1–O3 109.52(15), O1–Re1–O4 109.28(13), O2–Re–O3 109.31(13), O2–Re1–O4 108.88(12), O3–Re1–O4 109.14(13).

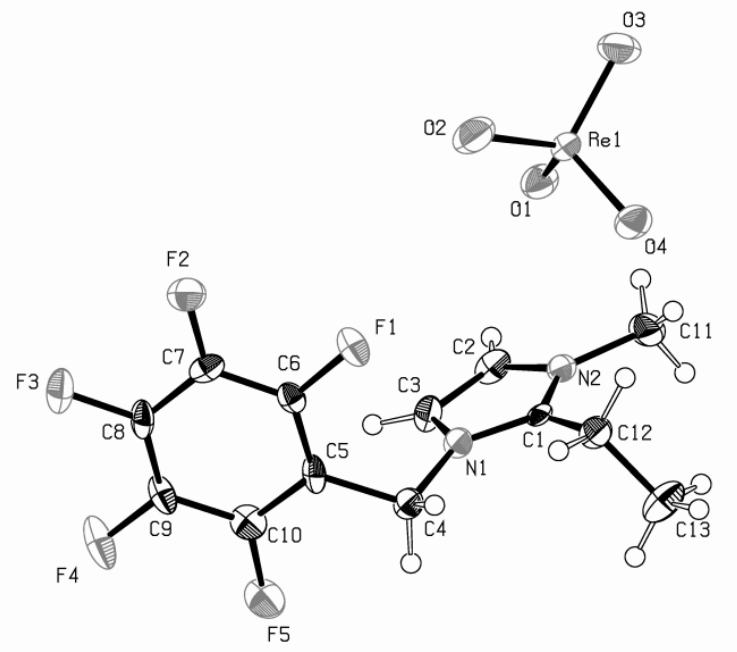


Figure S7. ORTEP style plot of compound **7** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.709(4), Re1–O2 1.707(5), Re1–O3 1.722(4), Re1–O4 1.726(4); O1–Re1–O2 109.7(2), O1–Re1–O3 109.26(18), O1–Re1–O4 109.0(2), O2–Re–O3 110.0(2), O2–Re1–O4 109.46(18), O3–Re1–O4 109.36(19).

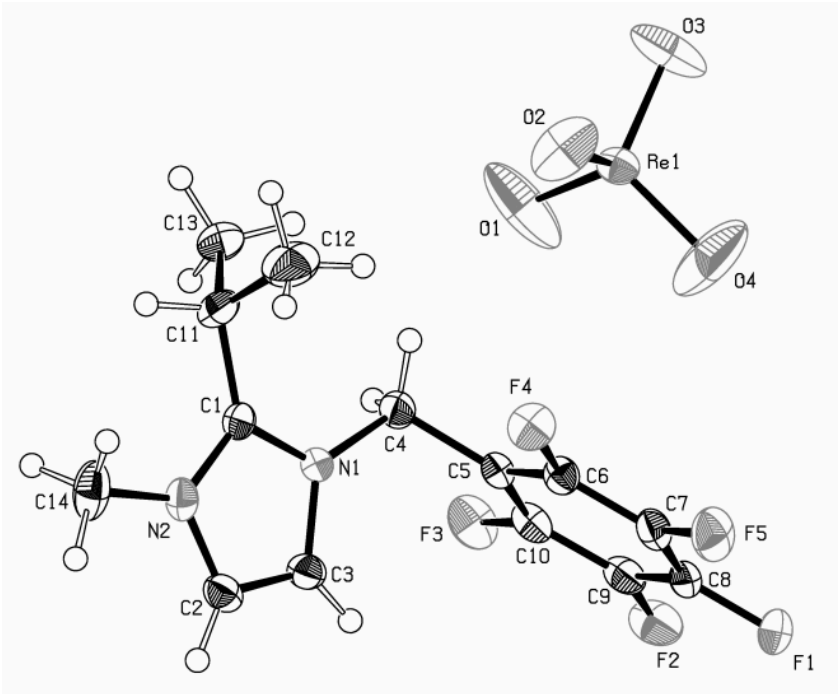


Figure S8. ORTEP style plot of compound **8** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.706(3), Re1–O2 1.702(2), Re1–O3 1.717(2), Re1–O4 1.684(3); O1–Re1–O2 108.13(15), O1–Re1–O3 108.72(13), O1–Re1–O4 110.1(2), O2–Re–O3 110.40(15), O2–Re1–O4 108.05(16), O3–Re1–O4 111.42(19).

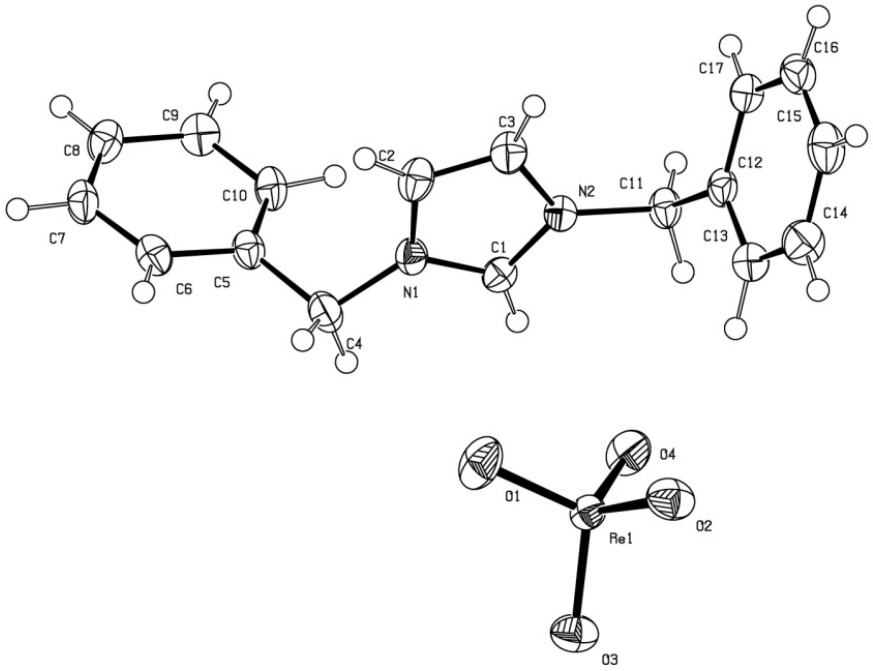


Figure S9. ORTEP style plot of compound **9** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.710(3), Re1–O2 1.723(3), Re1–O3 1.723(3), Re1–O4 1.721(3); O1–Re1–O2 109.16(14), O1–Re1–O3 110.74(14), O1–Re1–O4 108.76(14), O2–Re–O3 109.11(13), O2–Re1–O4 109.39(13), O3–Re1–O4 109.67(13).

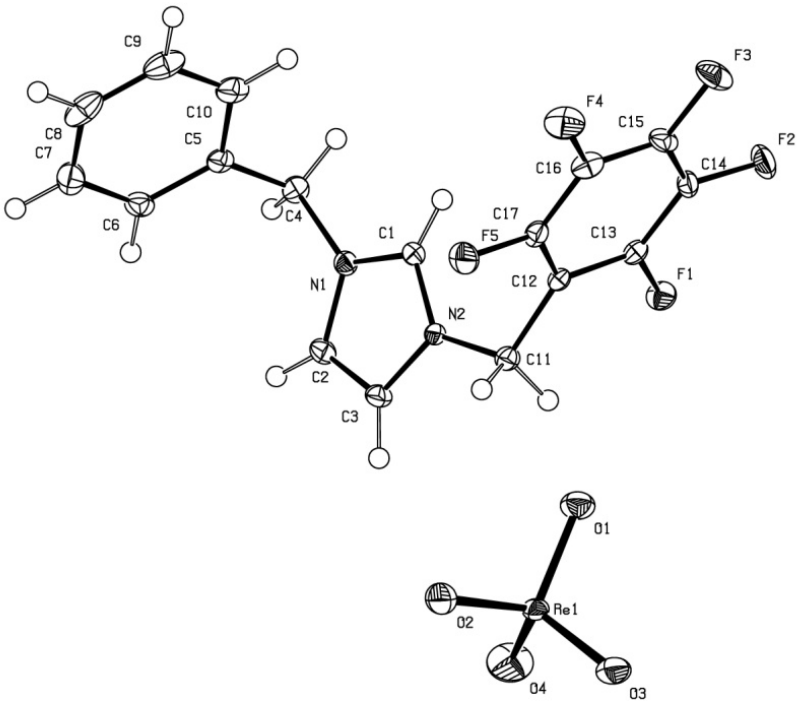


Figure S10. ORTEP style plot of compound **10**in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.7238(17), Re1–O2 1.7315(19), Re1–O3 1.7198(19), Re1–O4 1.713(2); O1–Re1–O2 109.34(8), O1–Re1–O3 109.71(9), O1–Re1–O4 109.38(10), O2–Re1–O3 109.34(9), O2–Re1–O4 109.89(10), O3–Re1–O4 109.16(10).

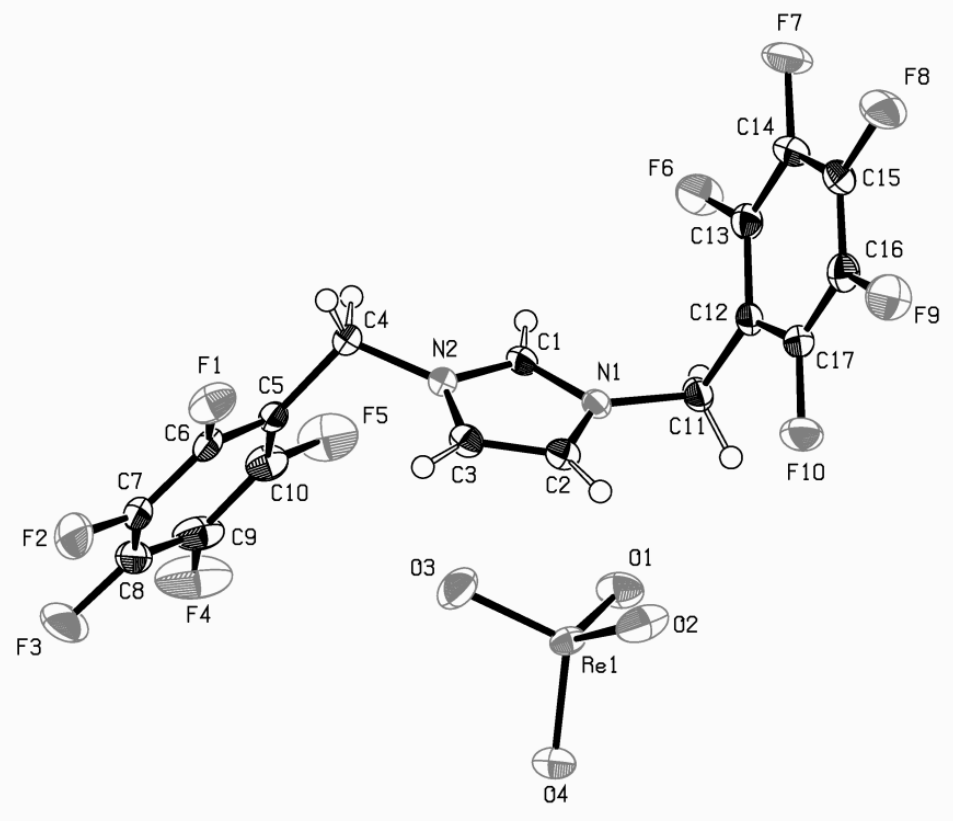
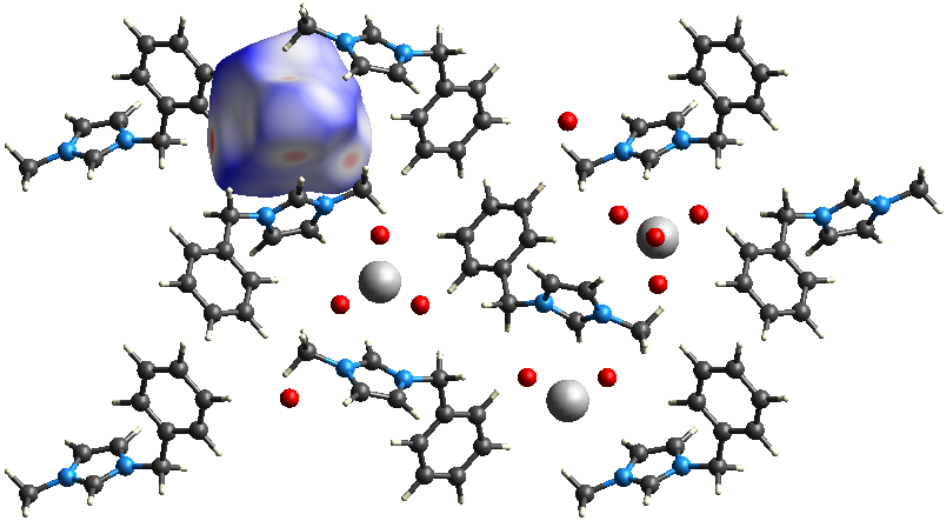


Figure S11. ORTEP style plot of compound **11**in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Re1–O1 1.7269(15), Re1–O2 1.7201(14), Re1–O3 1.7153(16), Re1–O4 1.7253(14); O1–Re1–O2 109.35(9), O1–Re1–O3 110.34(8), O1–Re1–O4 107.43(7), O2–Re1–O3 109.48(8), O2–Re1–O4 109.80(7), O3–Re1–O4 110.40(8).

2. Hirshfeld surface analysis

1-Benzyl-3-methylimidazolium perrhenate (**1**)



d_{norm}:

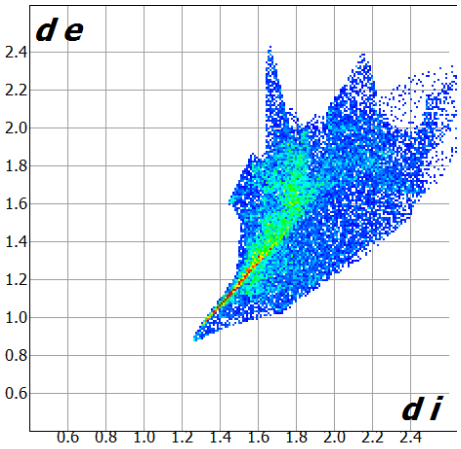
Min	-0.3733
Max	1.1694
Mean	0.3420
Mean+	0.3776
Mean-	-0.1051

interactions:

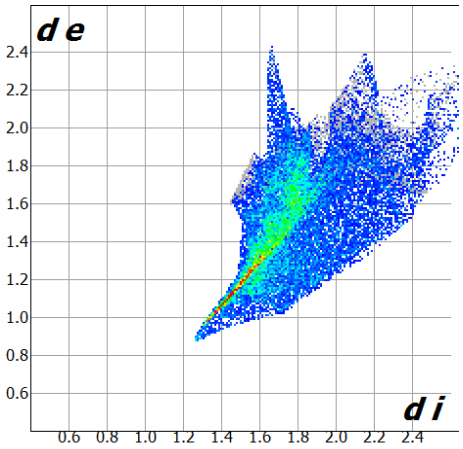
(O-C) = 7.4 %; (O-O) = 2.6 %; (O-N) = 4.1 %

fingerprint plots:

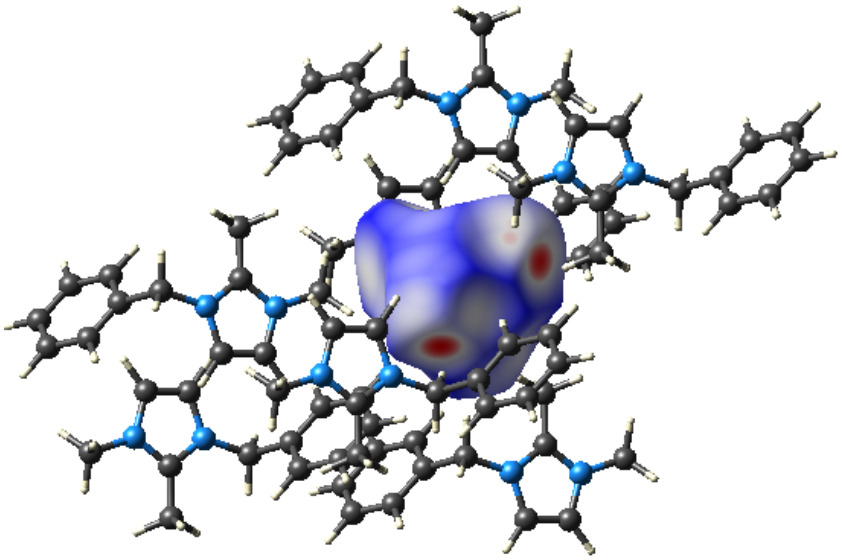
all contacts (99.8 %)



O-H interactions (85.6 % of all interactions)

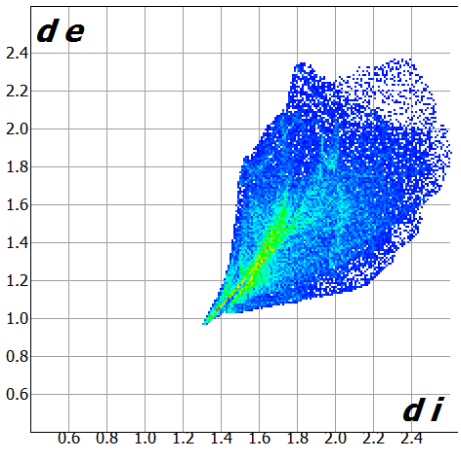


1-Benzyl-2,3-dimethylimidazolium perrhenate (**2**)



d_{norm}:	
Min	-0.2631
Max	0.9826
Mean	0.3425
Mean+	0.3708
Mean-	-0.0822

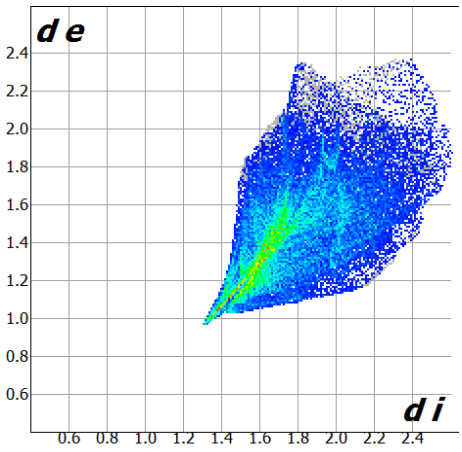
interactions:



(O-C) = 1.3 %; (O-O) = 3.0 %; (O-N) = 1.3 %

plots:

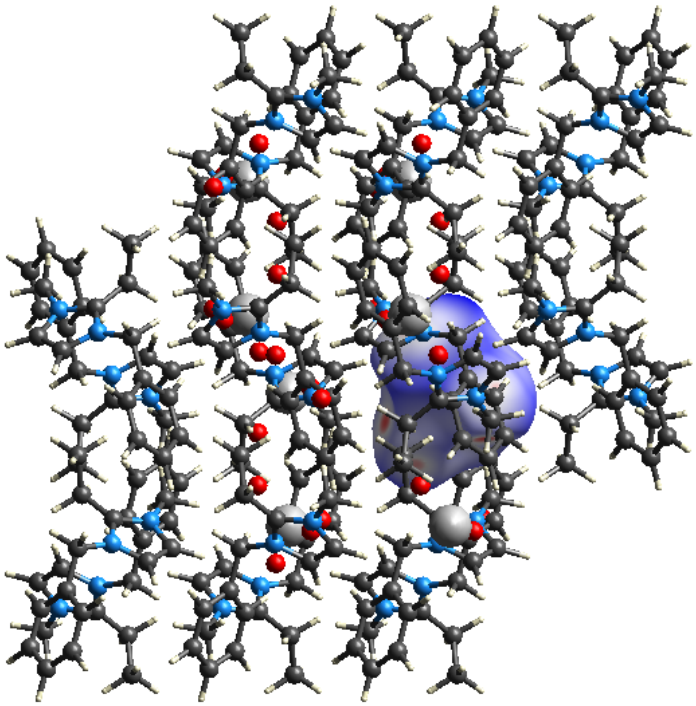
fingerprint



all contacts (100 %)

O-H interactions (94.2 % of all interactions)

1-Benzyl-2-ethyl-3-methylimidazolium perrhenate (**3**)



d_{norm}:

Min	-0.2253
Max	1.2911
Mean	0.3826
Mean+	0.4162
Mean-	-0.0739

interactions:

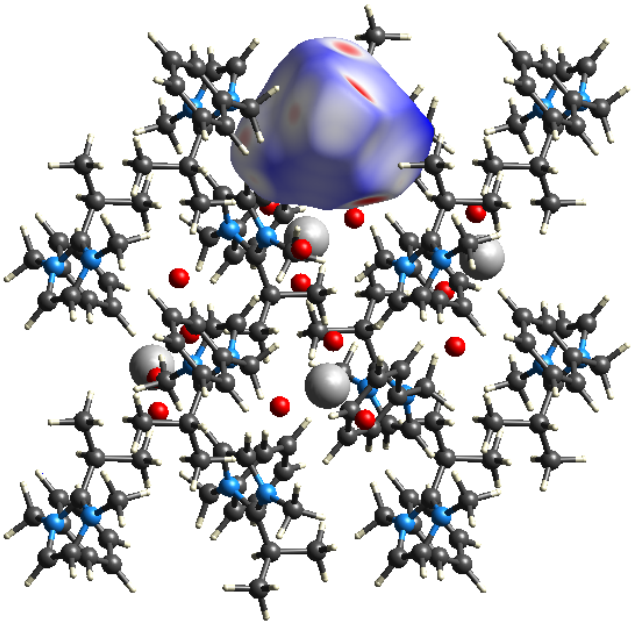
(O-C) = 1.9 %; (O-O) = 2.2 %; (O-N) = 2.2 %

fingerprint plots:

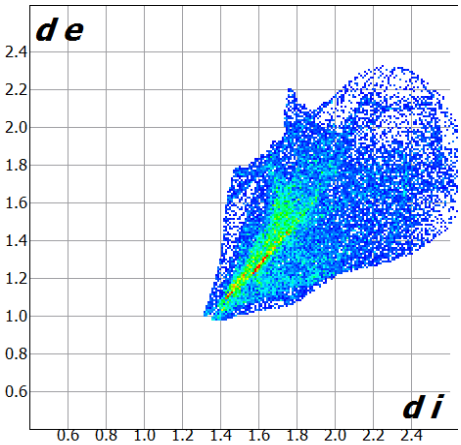
all contacts (99.6 %)

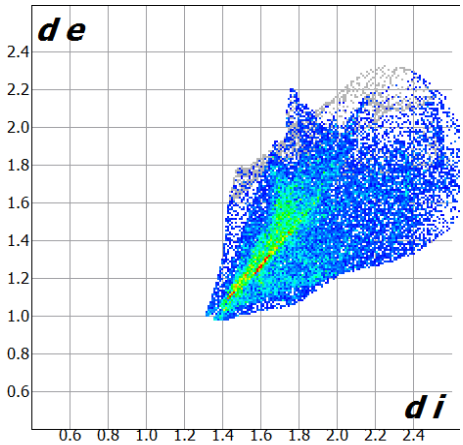
O-H interactions (93.2 % of all interactions)

1-Benzyl-2-isopropyl-3-methylimidazolium perrhenate (**4**)



d_{norm}:





Min -0.3590

Max	1.3398
Mean	0.3854
Mean+	0.4195
Mean-	-0.1271

interactions:

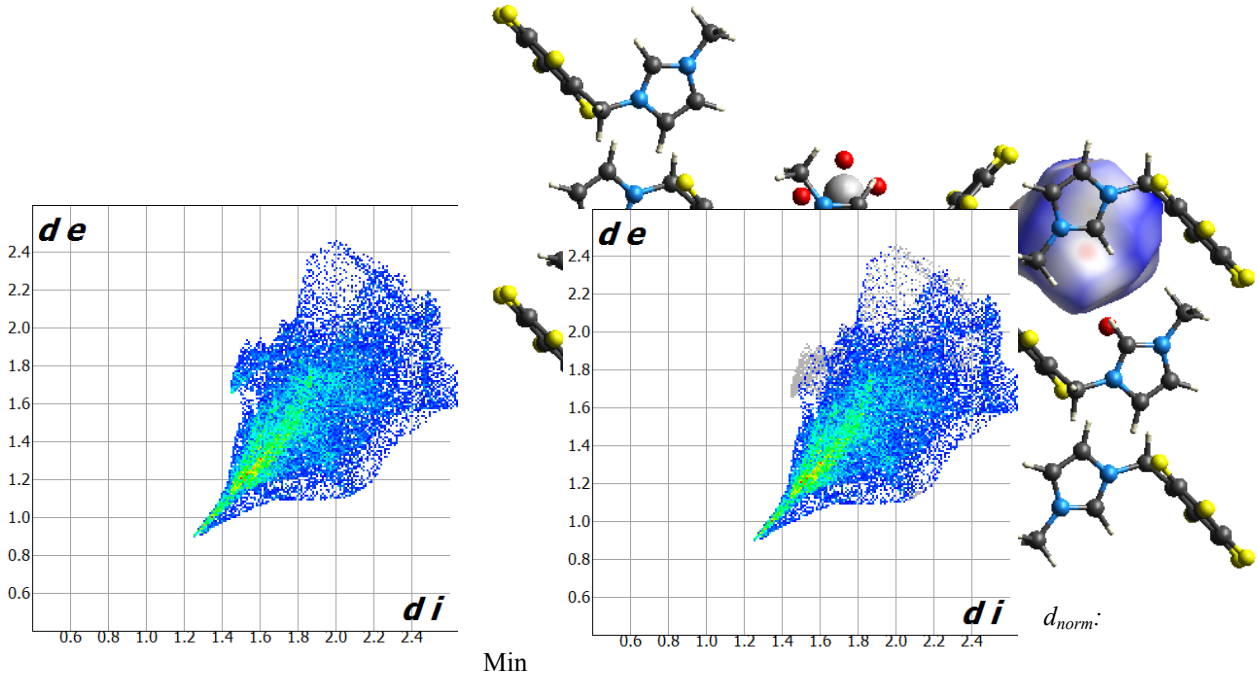
(O-C) = 4.0 %; (O-O) = 2.6 %; (O-N) = 2.8 %

fingerprint plots:

all contacts (99.2 %)

O-H interactions (89.8% of all interactions)

1-Methyl-3-(2',3',4',5',6'-pentafluorobenzyl)imidazolium perrhenate (**5**)



d_{norm}:

Min

-0,4307

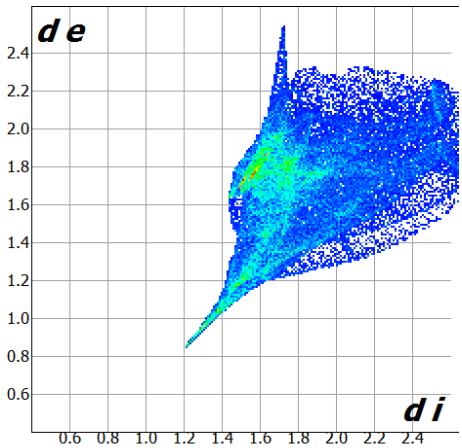
Max	1,2456
Mean	0,3481
Mean+	0,3824
Mean -	-0,1503

interactions:

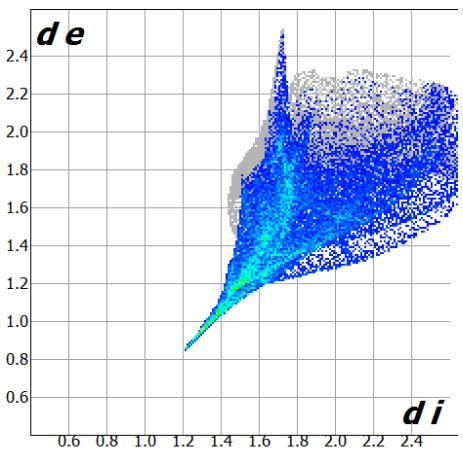
(O-F) = 16.5 %; (O-N) = 4.1 %; (O-O) = 5.4 %; (O-C) = 21.5 %

fingerprint plots:

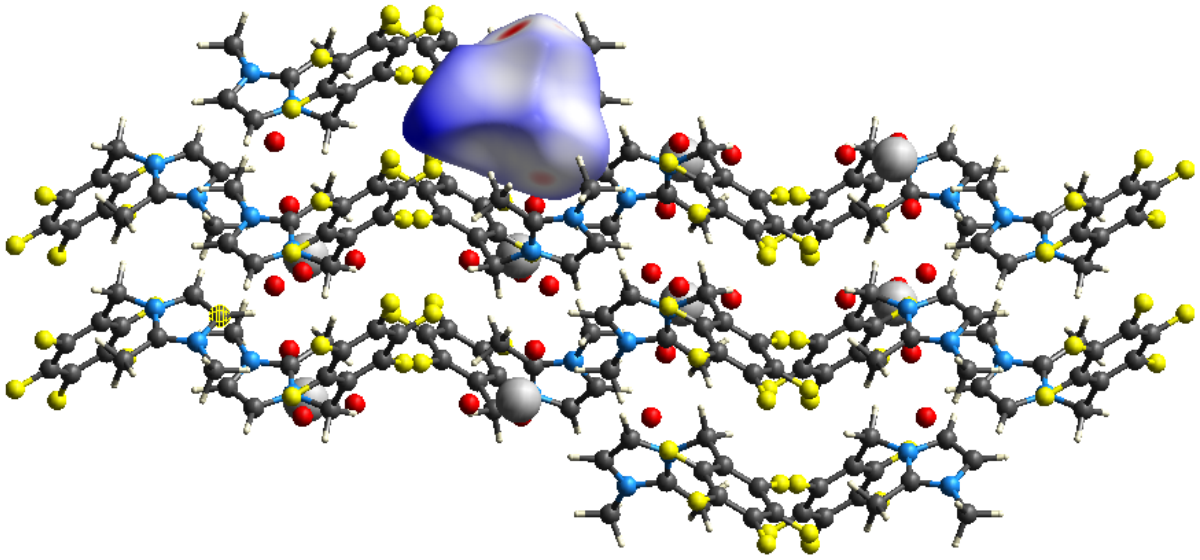
all contacts (98.7 %)



O-H interactions (51.3 % of all interactions)



1,2-Dimethyl-3-(2’,3’,4’,5’,6’-pentafluorobenzyl)imidazolium perrhenate (**6**)



d_{norm}

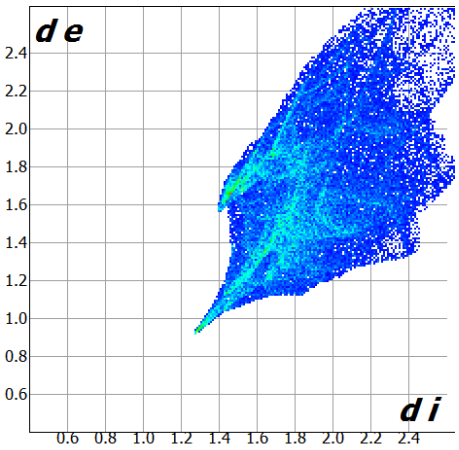
Min	-0,3293
Max	1,7083
Mean	0,4283
Mean+	0,4651
Mean-	-0,0889

interactions

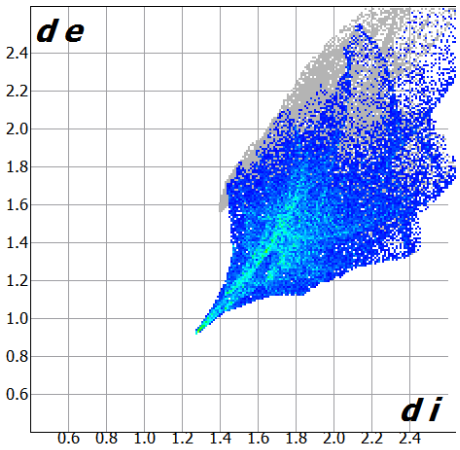
(O-F) = 18.7 %; (O-N) = 2.6 %; (O-O) = 0.0 %; (O-C) = 16.7 %

fingerprint plots:

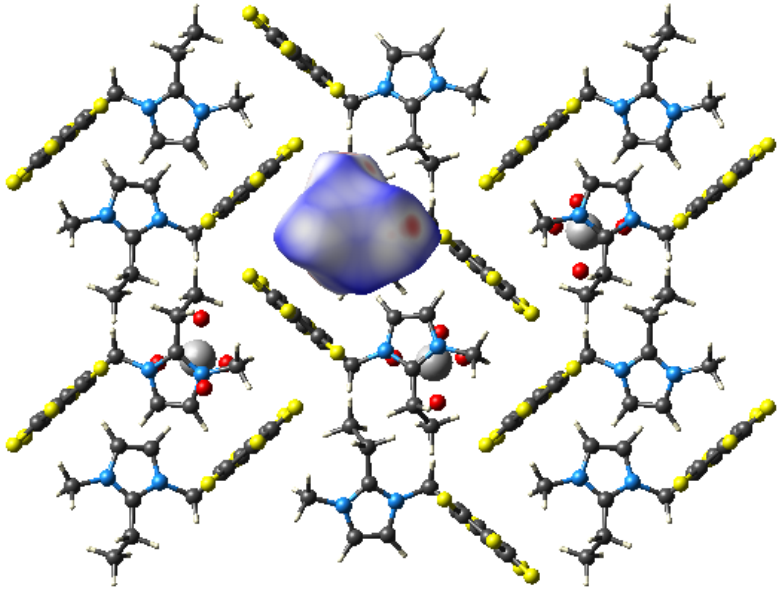
all contacts (97.0 %)



O-H interactions (59.8 % of all interactions)



2-Ethyl-1-methyl-3-(2’,3’,4’,5’,6’-pentafluorobenzyl)imidazolium perrhenate (**7**)



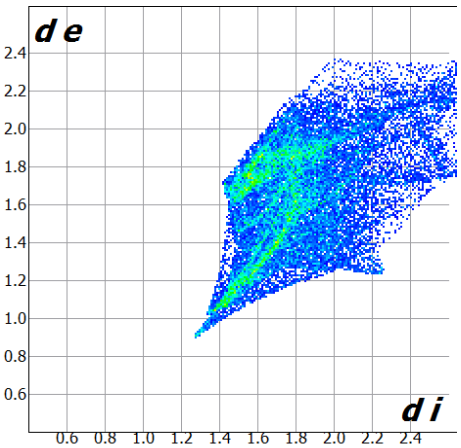
d_{norm}	
Min	-0.3468
Max	1.0485
Mean	0.3372
Mean+	0.3690
Mean-	-0.0765

interactions:

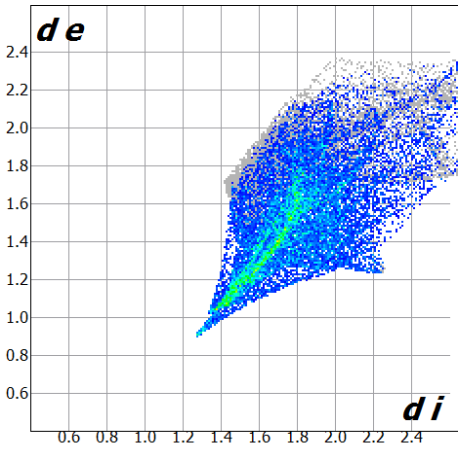
(O-F) = 12.2 %; (O-N) = 4.5 %; (O-O) = 0.0 %; (O-C) = 21.1 %

fingerprint plots:

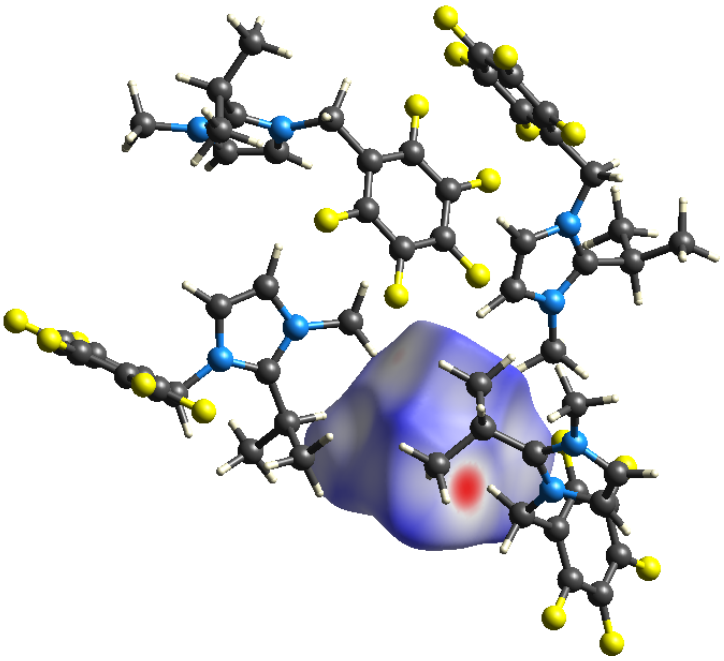
all contacts (98.8 %)



O-H interactions (61.1% of all interactions)



2-Isopropyl-1-methyl-3-(2’,3’,4’,5’,6’-pentafluorobenzyl)imidazolium perrhenate (**8**)



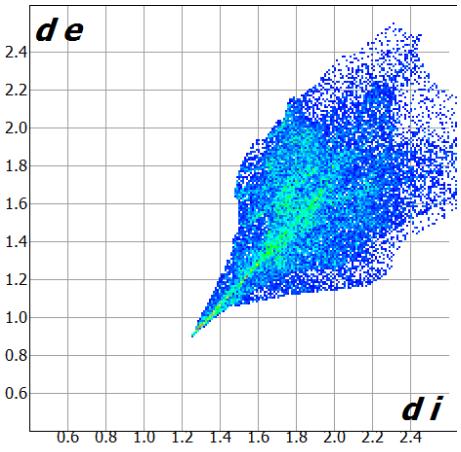
d_{norm}	
Min	-0.3580
Max	1.5508
Mean	0.4153
Mean+	0.4539
Mean-	-0.1171

interactions:

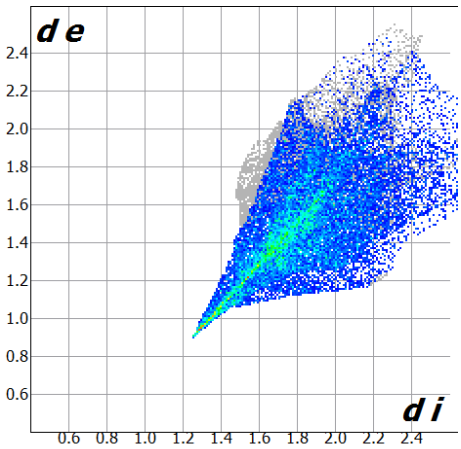
(O-F) = 16.6 %; (O-N) = 0.3 %; (O-O) = 0.0 %; (O-C) = 10.8 %

fingerprint plots:

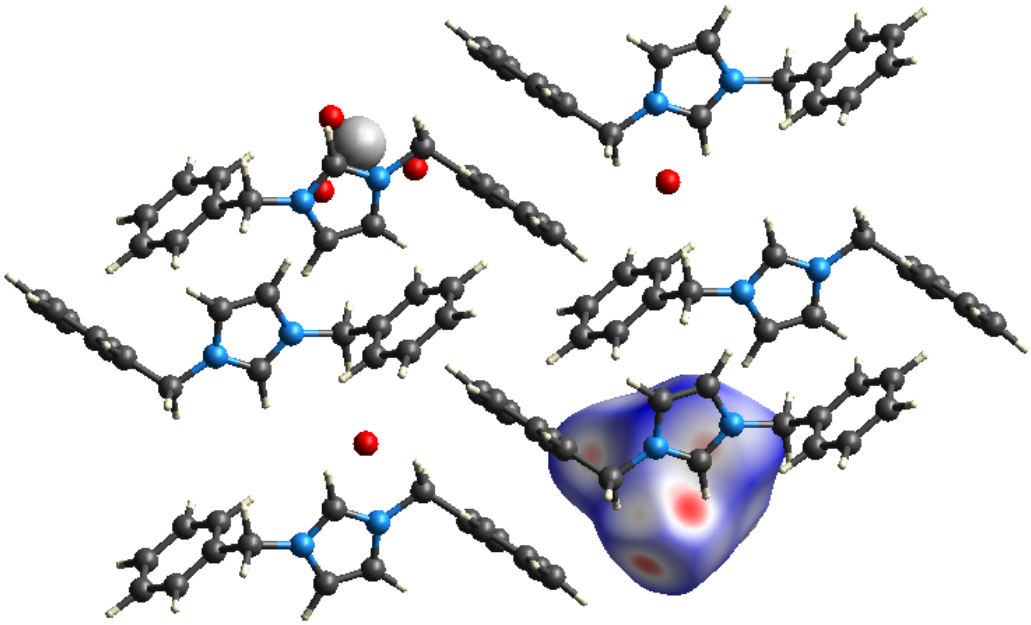
all contacts (97.0 %)



O-H interactions (69.1% of all interactions)



1,3-Dibenzylimidazolium perrhenate (**9**)



d_{norm}:

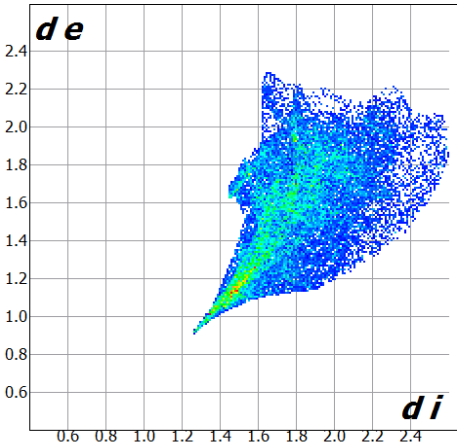
Min	-0.3399
Max	0.9828
Mean	0.3353
Mean+	0.3736
Mean-	-0.0889

interactions:

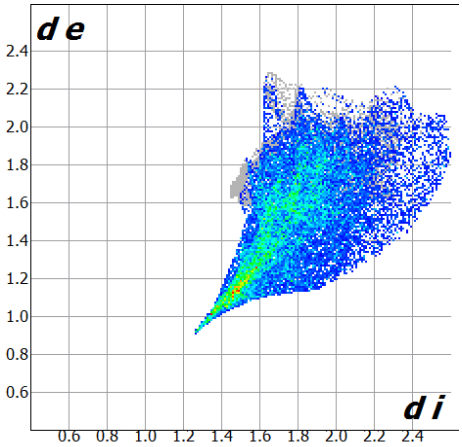
(O-C) = 9.4 %; (O-O) = 4.3 %; (O-N) = 2.7 %

fingerprint plots:

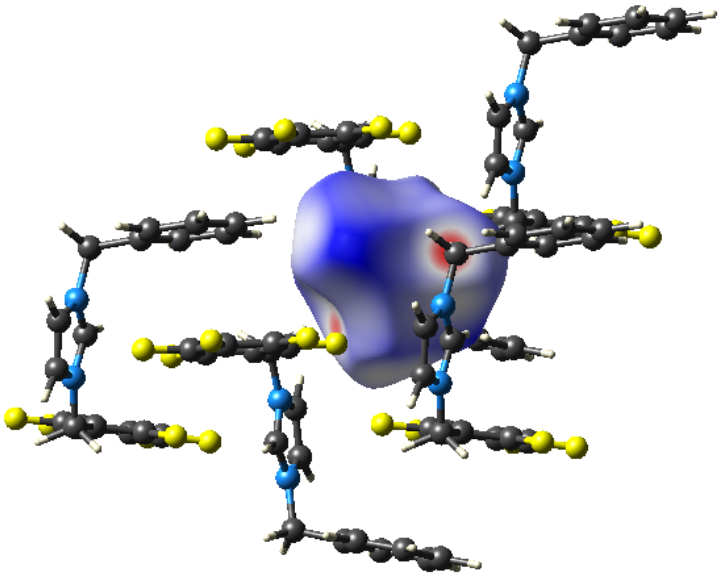
all contacts (100 %)



O-H interactions (83.4 % of all interactions)



1-Benzyl-3-(2’,3’,4’,5’,6’-pentafluorobenzyl)imidazolium perrhenate (**10**)



d_{norm}:

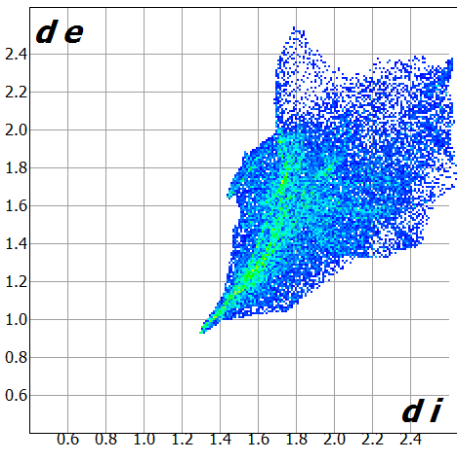
Min	-0.3118
Max	1.3007
Mean	0.3910
Mean+	0.4222
Mean-	-0.0987

interactions:

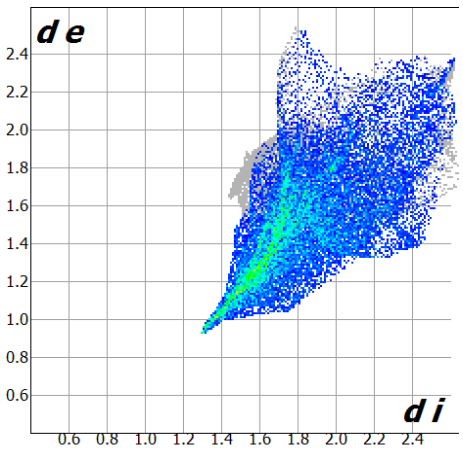
(O-C) = 6.0 %; (O-O) = 2.9 %; (O-N) = 0.0 %; (O-F) = 16.6 %

fingerprint plots:

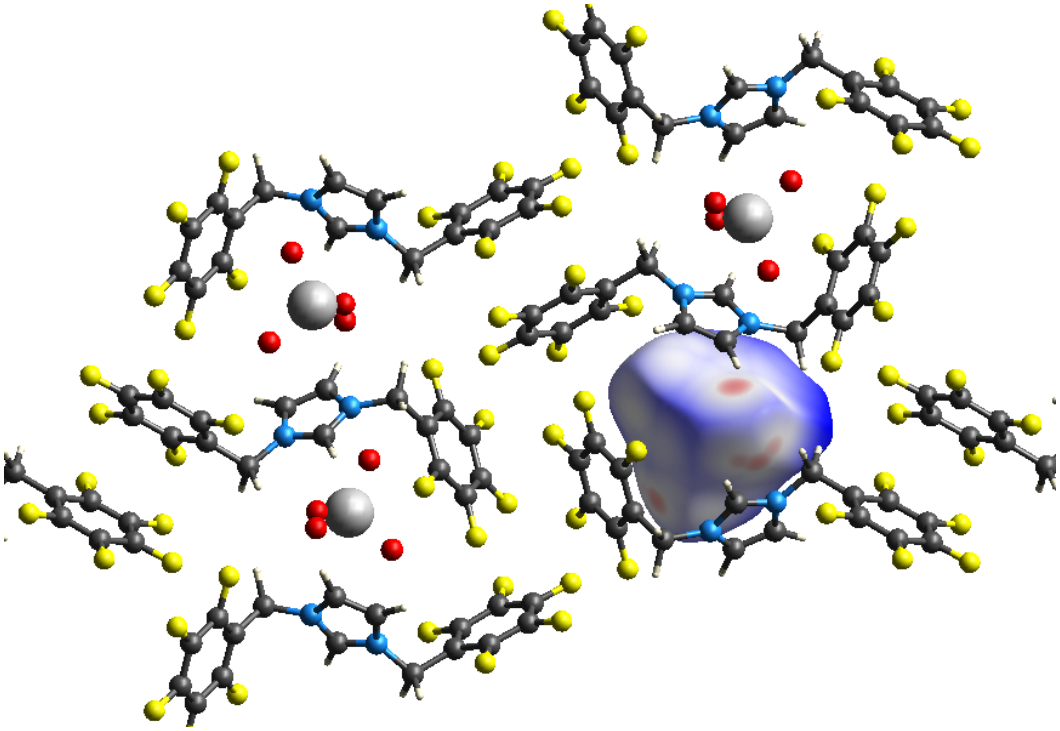
all contacts (100 %)



O-H interactions (74.5 % of all interactions)



Bis-(2’,3’,4’,5’,6’-pentafluorobenzyl)imidazolium perrhenate (**11**)



d_{norm}:

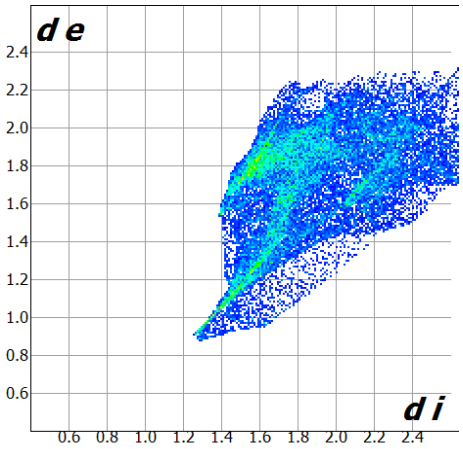
Min	-0.3548
Max	1.5213
Mean	0.3991
Mean+	0.4419
Mean-	-0.0994

interactions:

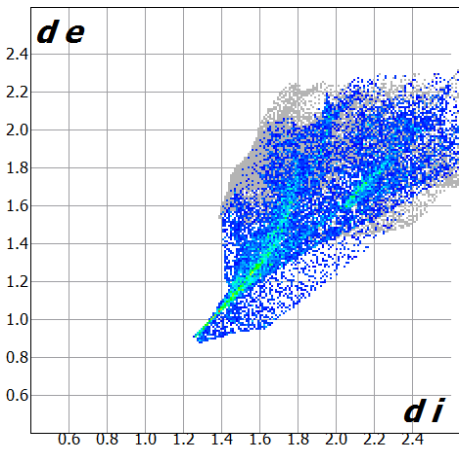
(O-F) = 20.7 %; (O-N) = 5.3 %; (O-O) = 0.1 %; (O-C) = 23.2 %

fingerprint plots:

all contacts (97.3 %)



O-H interactions (47.8% of all interactions)



3. Computational details

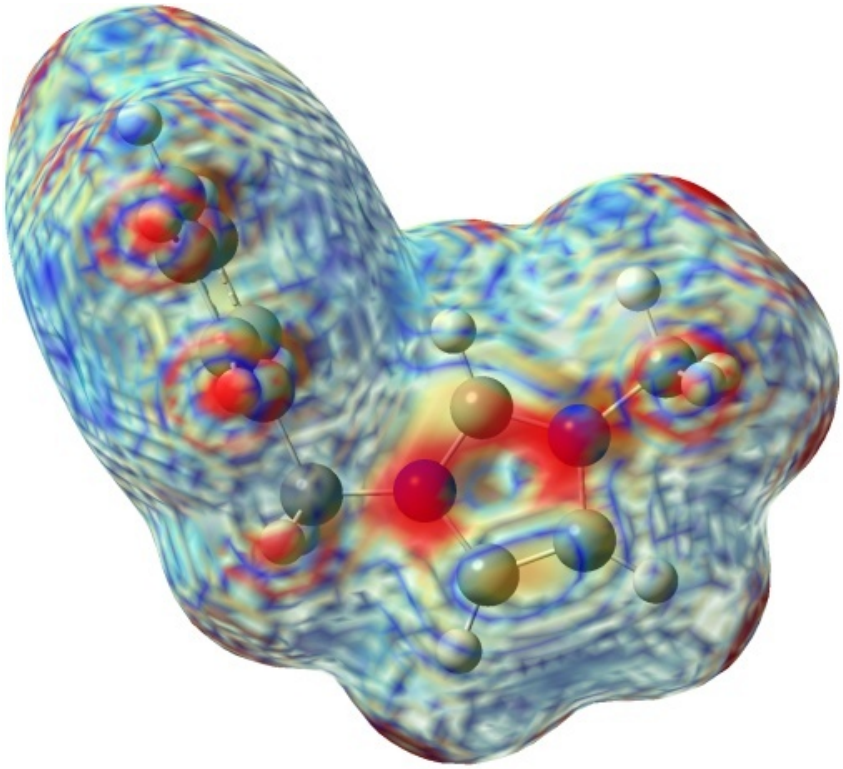


Figure S12. Distribution of charge density for 1-benzyl-3-methylimidazolium (cation of compound **1**).

C	1.29017000	0.45025900	-0.00012500
C	2.40007600	-1.45503700	0.00010800
C	3.30921200	-0.44281300	0.00009300
H	0.48431500	1.16412500	-0.00022200
H	2.53964100	-2.52282100	0.00022500
H	4.38592200	-0.46451500	0.00015400
N	2.59622500	0.74122200	-0.00006200
N	1.14437800	-0.87712700	-0.00003700
C	3.17541600	2.09245300	-0.00007000
H	3.78526200	2.22706500	-0.89293100
H	2.36817700	2.82198900	-0.00019200
H	3.78508400	2.22716000	0.89289700
C	-0.14936400	-1.63426800	-0.00004000
H	-0.13080300	-2.27163500	0.88535900
H	-0.13081000	-2.27163700	-0.88544000
C	-1.35364300	-0.73127100	-0.00002300
C	-1.91942600	-0.30950800	-1.20871600
C	-1.91925700	-0.30940300	1.20871700
C	-3.03039800	0.53092400	-1.20794600
H	-1.50340000	-0.65039800	-2.15162100
C	-3.03023000	0.53102600	1.20804200
H	-1.50309000	-0.65021200	2.15159000
C	-3.58424700	0.95331200	0.00006800
H	-3.47032800	0.84421200	-2.14719800
H	-3.47003100	0.84438500	2.14733000
H	-4.45401400	1.59957600	0.00009500

Sum of electronic and thermal Enthalpies = -536.186840
Sum of electronic and thermal Free Energies = -536.238517
(in Hartree)

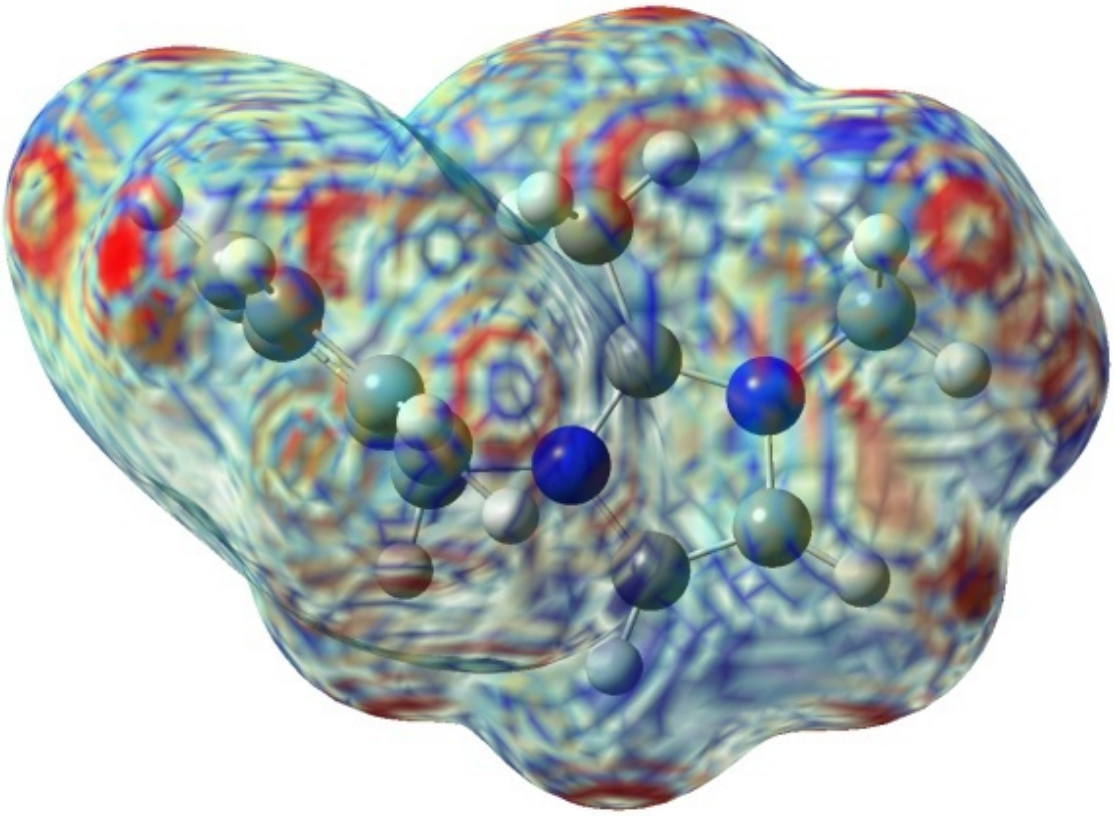


Figure S13. Distribution of charge density for 1-benzyl-2,3-dimethylimidazolium (cation of compound **2**).

C	-1.57420700	-0.53489100	-0.22890800
C	-1.81797900	1.66906600	-0.41059100
C	-2.89607200	1.18889300	0.25850200
H	-1.56189500	2.67298900	-0.70230800
H	-3.75637500	1.69394200	0.66230300
N	-2.73050700	-0.18113200	0.36468100
N	-1.00649500	0.58912400	-0.70650200
C	-3.68238300	-1.09205100	1.01786100
H	-4.49363600	-0.49494100	1.42763900
H	-4.09098500	-1.79556900	0.29268100
H	-3.19363700	-1.62921800	1.83002500
C	0.29477100	0.67307600	-1.41533000
H	0.35281000	1.69445000	-1.79623600
H	0.24967700	0.00974200	-2.28090300
C	1.48611700	0.33902700	-0.54191500
C	2.44704100	-0.56327300	-1.00420200
C	1.66817200	0.95951200	0.69902000
C	3.57722400	-0.84384800	-0.23695400
H	2.32256000	-1.04327000	-1.96972200
C	2.79252100	0.67249100	1.46799000
H	0.93896100	1.67342200	1.06891100
C	3.74916900	-0.22918500	1.00066500
H	4.31941300	-1.54113000	-0.60695100
H	2.92778100	1.15934300	2.42655200
H	4.62640100	-0.44683000	1.59815500
C	-1.02120500	-1.90847500	-0.34344800
H	-0.85035400	-2.16934000	-1.39136300
H	-0.06391400	-1.98106300	0.17855700
H	-1.70682100	-2.64053000	0.07926200

Sum of electronic and thermal Enthalpies = -575.491683
Sum of electronic and thermal Free Energies = -575.547321
(in Hartree)

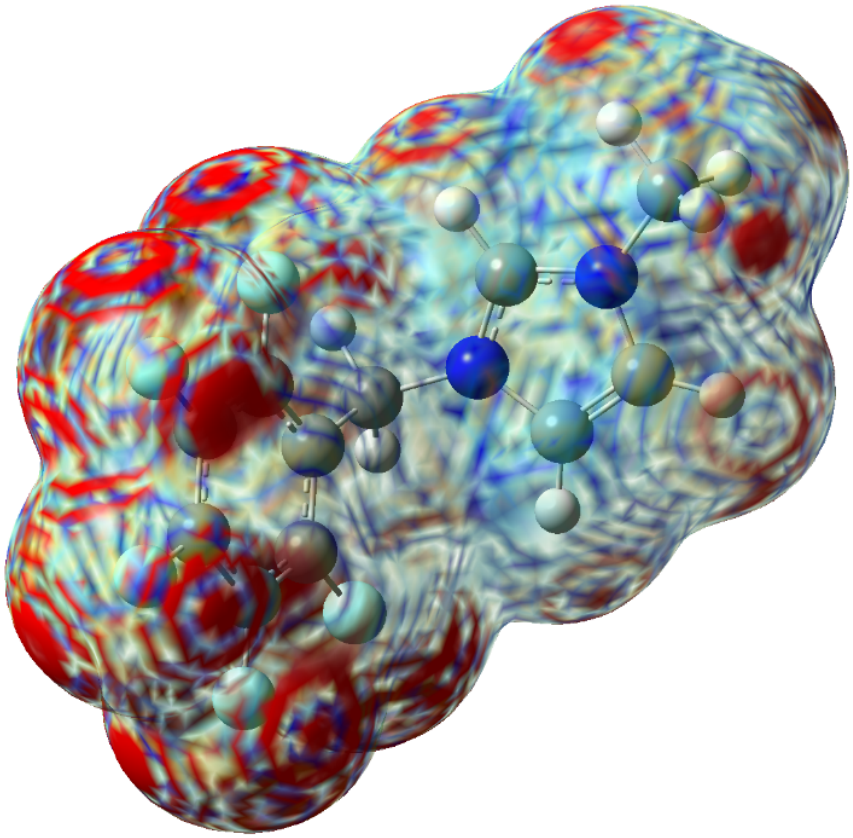


Figure S14. Distribution of charge density for the cation 1-pentafluorobenzyl-3-methylimidazolium (cation of compound **5**).

C	-2.84505798	-0.58161694	-0.36874277
C	-2.49499669	1.52029145	0.21419294
C	-3.56791583	1.06221190	0.91411219
H	-2.01305122	2.48354293	0.21375833
H	-4.19917581	1.55521006	1.63404042
N	-3.77062967	-0.25274052	0.53628996
N	-2.05876935	0.47932798	-0.58474090
C	-4.83485571	-1.13535741	1.04083276
H	-4.73454155	-1.24118299	2.12047972
H	-5.80641435	-0.70833476	0.79436361
H	-4.73723424	-2.11140634	0.57008817
C	-0.88515938	0.51204970	-1.49594967
H	-0.86508264	1.50009088	-1.95180002
H	-1.06988535	-0.21915850	-2.28151617
C	0.41380891	0.22242363	-0.79031453
C	0.83815250	-1.08757011	-0.57641009
C	1.24978483	1.24684516	-0.35079424
C	2.04730376	-1.38186479	0.03620583
C	2.46765737	0.98741850	0.26486454
C	2.86543042	-0.33412364	0.45700007
F	0.04537194	-2.10025708	-0.97537245
F	0.87074249	2.52311149	-0.52414840
F	3.24496242	1.98242946	0.67272317
F	4.02005457	-0.59638079	1.04653836
F	2.42401707	-2.64055379	0.22596569
H	-2.74007124	-1.54426183	-0.84159706

Sum of electronic and thermal Enthalpies = -1032.516981
Sum of electronic and thermal Free Energies = -1032.579639
(in Hartree)

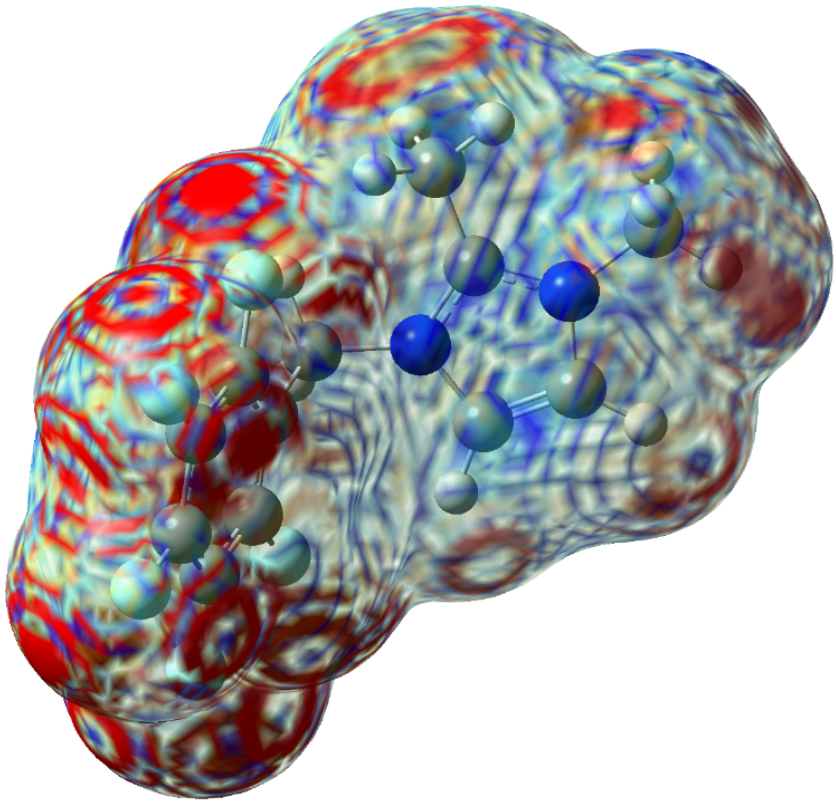


Figure S15. Distribution of charge density for the cation 1-pentafluorobenzyl-2,3-dimethylimidazolium (cation of compound **6**).

C	-2.87239988	-0.36899399	-0.21474806
C	-2.04926964	1.65772001	0.22232185
C	-3.17722894	1.50085246	0.95666827
H	-1.36570033	2.48587829	0.14595414
H	-3.66538422	2.16857295	1.64552610
N	-3.67773633	0.24074439	0.67519751
N	-1.87207001	0.48910272	-0.50086696
C	-4.90197779	-0.32538803	1.26316232
H	-5.34604671	0.42923480	1.90802248
H	-5.61239770	-0.58347533	0.47856972
H	-4.66218351	-1.20543107	1.85972570
C	-0.74966878	0.25472263	-1.44271839
H	-0.71867934	1.10742498	-2.11993010
H	-0.98973074	-0.62904737	-2.02853821
C	0.58135354	0.08570129	-0.75228245
C	1.05033544	-1.16829878	-0.36640750
C	1.40993042	1.17841544	-0.50239911
C	2.28914913	-1.34198064	0.23495676
C	2.65458308	1.04104437	0.09726582
C	3.09437648	-0.22848277	0.46634490
F	0.28294871	-2.25254750	-0.58447957
F	0.99156450	2.40934083	-0.84616455
F	3.41840047	2.10280420	0.32237627
F	4.27587203	-0.37667405	1.04262626
F	2.70646479	-2.55173389	0.58851578
C	-3.07498844	-1.72392588	-0.79319936
H	-2.14217183	-2.28882461	-0.80085297
H	-3.80283512	-2.28423595	-0.20843248
H	-3.44864829	-1.65804949	-1.82001635

Sum of electronic and thermal Enthalpies = -1071.823873
Sum of electronic and thermal Free Energies = -1071.889234
(in Hartree)

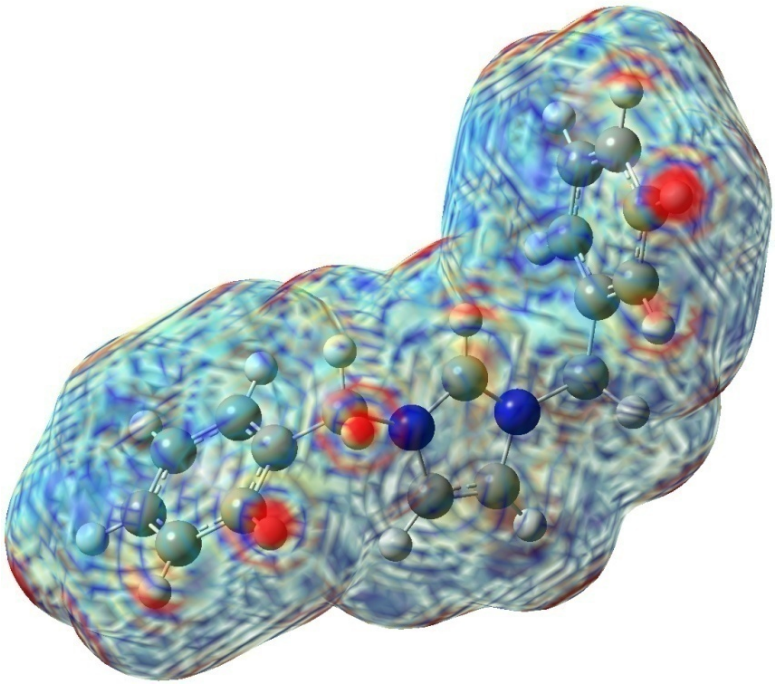


Figure S16. Distribution of charge density for 1,3-dibenzylimidazolium (cation of compound **9**).

C	0.03750000	2.24624700	0.70812900
C	-1.09724100	1.75362100	0.14070900
C	0.53332800	0.31337300	-0.22869900
N	1.04652400	1.33229700	0.46736000
H	0.20797100	3.15515300	1.25983000
H	-2.09927500	2.14544600	0.11242300
H	1.08384700	-0.54830800	-0.56504000
N	-0.76704300	0.54464700	-0.43954000
C	2.45867300	1.46753200	0.94477800
H	2.79622200	2.45309900	0.62033300
H	2.42177400	1.45784400	2.03537600
C	3.35978700	0.38088300	0.42070300
C	3.98739800	0.52247800	-0.82250400
C	3.58059800	-0.77731200	1.17399100
C	4.81629000	-0.48530000	-1.30914500
H	3.84150400	1.42690200	-1.40479200
C	4.41051500	-1.78491800	0.68629400
H	3.11745800	-0.88636700	2.14965600
C	5.02624400	-1.64020300	-0.55598600
H	5.30784800	-0.36398300	-2.26706600
H	4.58547200	-2.67411700	1.28013900
H	5.67860900	-2.41990400	-0.93101700
C	-1.68334400	-0.33324300	-1.22663000
H	-1.77101200	0.10034000	-2.22427500
H	-1.17464000	-1.29419800	-1.31809500
C	-3.03812400	-0.48041000	-0.58108200
C	-4.14885300	0.16557200	-1.13049900
C	-3.19833000	-1.27179300	0.56220800
C	-5.40489600	0.02973700	-0.53998300
H	-4.03930500	0.76444200	-2.02922600
C	-4.45105100	-1.40448000	1.15253400
H	-2.34688400	-1.79390200	0.98776400
C	-5.55550000	-0.75230600	0.60228200
H	-6.26244100	0.52783700	-0.97633100
H	-4.56962300	-2.02361000	2.03379800
H	-6.53185400	-0.86215500	1.05917800

Sum of electronic and thermal Enthalpies = -767.212206
Sum of electronic and thermal Free Energies = -767.276035
(in Hartree)

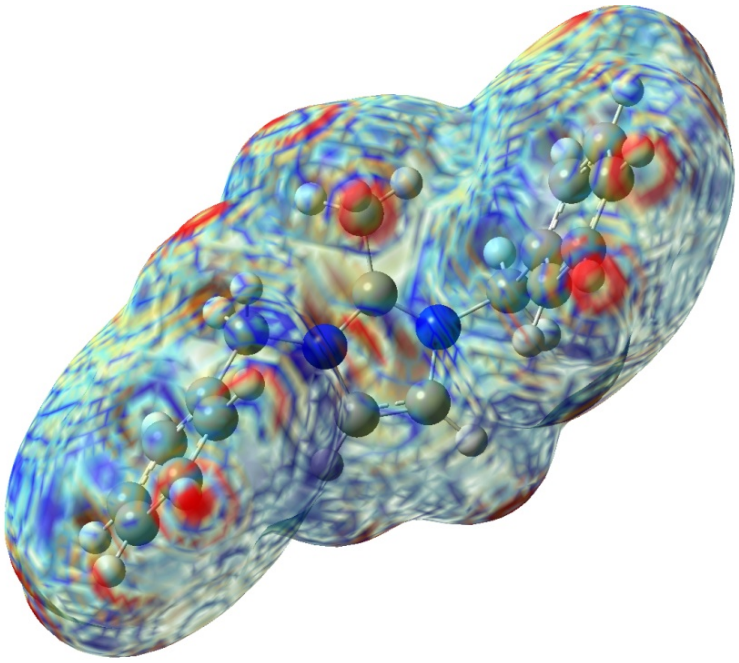


Figure S17. Distribution of charge density for 1,3-dibenzyl-2-methylimidazolium.

C	-0.13040800	-0.91280400	-1.77952200
C	1.08600700	-0.68636200	-1.22177000
C	-0.36771300	-1.03936300	0.42636500
N	-1.02451200	-1.13069000	-0.74594300
H	-0.43513900	-0.93932500	-2.81141700
H	2.04018300	-0.47282100	-1.66917900
N	0.92160200	-0.76577200	0.14870400
C	-2.47462100	-1.38225200	-0.92732700
H	-2.60669500	-1.55105100	-1.99788000
H	-2.72363000	-2.31862500	-0.42552800
C	1.99791200	-0.61984400	1.17765300
H	1.58091400	-0.01373900	1.98302700
H	2.20750500	-1.61642100	1.57196300
C	-3.35718000	-0.25344600	-0.43568000
C	-3.09437100	1.07522100	-0.78559500
C	-4.48515000	-0.54857400	0.33354200
C	-3.94548300	2.09310800	-0.36383200
H	-2.22975300	1.32222000	-1.39342300
C	-5.34110100	0.47063100	0.74939200
H	-4.70623900	-1.57680200	0.60262200
C	-5.07052500	1.79225400	0.40410200
H	-3.73652400	3.11941100	-0.64189300
H	-6.21565700	0.23037500	1.34222000
H	-5.73440900	2.58502900	0.72766800
C	3.25129900	0.01064400	0.62885700
C	3.35536500	1.40243600	0.52503700
C	4.32641800	-0.78975800	0.23042700
C	4.51498100	1.98377600	0.01983900
H	2.53473700	2.03482900	0.84904300
C	5.48772000	-0.20704400	-0.27407200
H	4.26367500	-1.86931700	0.32410300
C	5.58130600	1.17905700	-0.38178300
H	4.59147500	3.06232300	-0.05006500
H	6.31926600	-0.83387400	-0.57328900
H	6.48642400	1.63263500	-0.76800600
C	-0.94143600	-1.20134900	1.78768100
H	-1.00293400	-0.23670100	2.30065300
H	-1.94764100	-1.61143200	1.73889800
H	-0.32330700	-1.86948100	2.39127000

Sum of electronic and thermal Enthalpies = -806.516290
Sum of electronic and thermal Free Energies = -806.584377
(in Hartree)

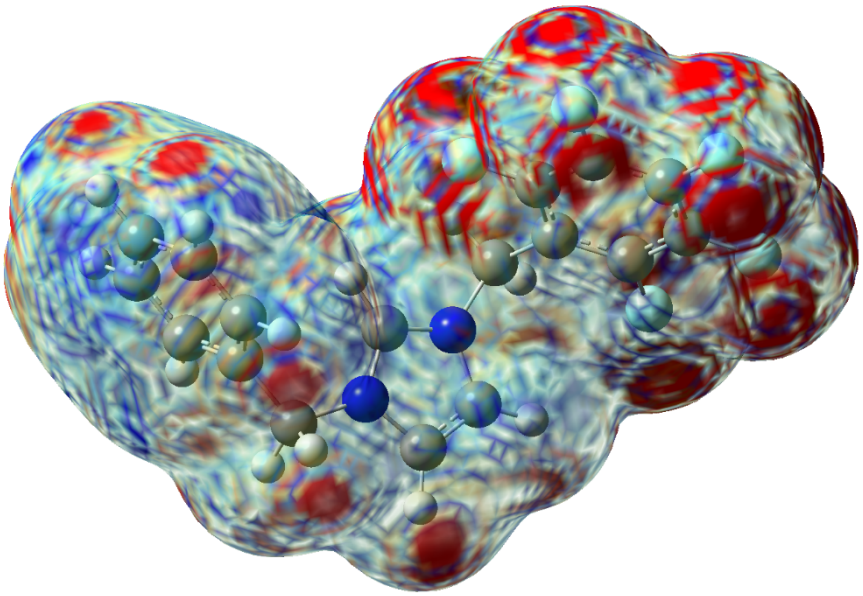


Figure S18. Distribution of charge density for the cation 1-benzyl-3-pentafluorobenzylimidazolium (cation of compound **10**).

C	1.31594444	2.75621007	0.99523729
C	0.17657103	2.67988300	0.25636698
C	1.46213042	0.96196795	-0.28045110
N	2.10533017	1.67536806	0.64564268
H	1.63019383	3.48246247	1.72570500
H	-0.68782229	3.32165699	0.22369584
H	1.82848768	0.05936396	-0.73939523
N	0.28772190	1.55286416	-0.53792643
C	3.45691036	1.37786351	1.22305107
H	4.06003177	2.27271271	1.06196729
H	3.31008696	1.24817431	2.29646620
C	4.09995375	0.16479671	0.60675505
C	4.89717656	0.29329016	-0.53656855
C	3.90917170	-1.10021318	1.17413205
C	5.48706895	-0.83056417	-1.11018804
H	5.07143056	1.27304144	-0.97031759
C	4.49959022	-2.22342638	0.59914206
H	3.31271100	-1.20784500	2.07468033
C	5.28648076	-2.08908725	-0.54389103
H	6.11203649	-0.72268250	-1.98862587
H	4.35565995	-3.19838230	1.04920406
H	5.75272969	-2.96181585	-0.98557421
C	-0.73609015	1.05523853	-1.48935987
H	-1.12755843	1.92076786	-2.02114703
H	-0.22181691	0.41971433	-2.20834416
C	-1.84911316	0.29831307	-0.81162346
C	-3.03562409	0.92619559	-0.43851559
C	-1.73897298	-1.06692484	-0.55473181
C	-4.08072371	0.23088649	0.15565748
C	-2.76371075	-1.79104785	0.03766725
C	-3.94130763	-1.13505492	0.39204782
F	-3.17655036	2.24466268	-0.65432698
F	-5.20017606	0.85564737	0.50044997
F	-4.92673750	-1.81058855	0.96130421
F	-2.62949453	-3.09214980	0.26896373
F	-0.60262701	-1.70365536	-0.88980139

Sum of electronic and thermal Enthalpies = -1263.544196
Sum of electronic and thermal Free Energies = -1263.618306
(in Hartree)

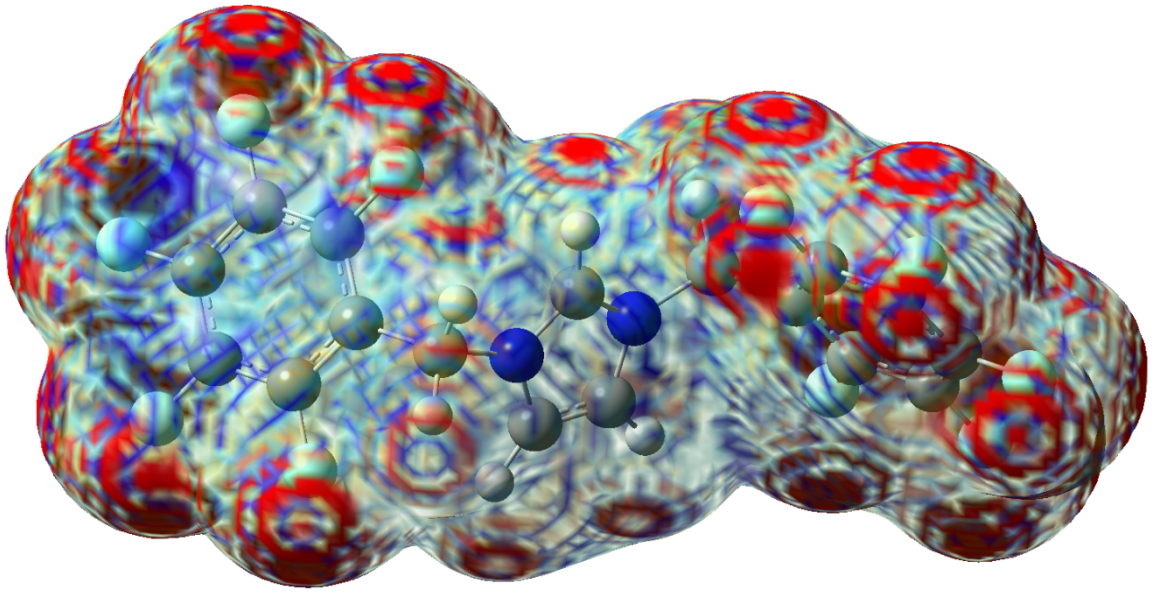


Figure S19. Distribution of charge density for the cation 1,3-bis(pentafluorobenzyl)imidazolium (cation of compound **11**).

C	0.53026738	1.64157576	0.42545238
C	-0.53046266	1.64153505	-0.42575260
C	-0.00002140	-0.46163073	-0.00015398
N	0.84439118	0.31842088	0.68233634
H	1.08294881	2.45605017	0.86287215
H	-1.08321456	2.45597019	-0.86315379
H	0.00005340	-1.53931408	-0.00016781
N	-0.84447324	0.31835561	-0.68265439
C	1.96557563	-0.16067347	1.53236529
H	1.98996897	0.47467144	2.41577173
H	1.71466813	-1.17207257	1.84866900
C	3.29189762	-0.13501481	0.81897434
C	4.18851349	0.91891953	0.98285530
C	3.67882181	-1.18274747	-0.01449321
C	5.42932280	0.93088698	0.35843340
C	4.90931474	-1.20136642	-0.65445221
C	5.78847741	-0.13625209	-0.46237912
C	-1.96570107	-0.16081184	-1.53258970
H	-1.99015244	0.47447763	-2.41603450
H	-1.71479262	-1.17222212	-1.84884316
C	-3.29196927	-0.13512087	-0.81909683
C	-4.18858004	0.91882093	-0.98290888
C	-3.67880520	-1.18281041	0.01447257
C	-5.42930174	0.93084721	-0.35830173
C	-4.90920889	-1.20136368	0.65460202
C	-5.78837914	-0.13623887	0.46260402
F	-3.84662306	1.95662343	-1.76330972
F	-6.26475911	1.94682624	-0.53326949
F	-6.96408616	-0.13572924	1.06857710
F	-5.24969824	-2.21370352	1.44292591
F	-2.82757080	-2.20775574	0.20610144
F	2.82759576	-2.20769270	-0.20617848
F	5.24989895	-2.21374834	-1.44267732
F	6.96426566	-0.13579414	-1.06819793
F	6.26479165	1.94683952	0.53345233
F	3.84646599	1.95676506	1.76316799

Sum of electronic and thermal Enthalpies = -1759.874415
Sum of electronic and thermal Free Energies = -1759.959324
(in Hartree)